VII.6 Carbon Ionic Conductors for Use in Novel Carbon-Ion Fuel Cells

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Objectives

- To evaluate the possibility that ionic carbides could act as superionic membrane materials for carbon ions, allowing the development of a radically new fuel cell based on the transport of carbon ions rather than hydrogen or oxygen ions.

Approach

- Stabilization of the fluorite crystal structure via combining at least two lanthanides having substantially different ionic radii.
- Preparation of pseudo-binary ionic carbide compounds using carbon-13 together with the diffusion of carbon-12 vapor-deposited layers.
- Analysis of the in-diffusion profiles of carbon-12 into pseudo-binary ionic carbide compounds using SIMS (secondary ion mass spectrometry) to determine carbon ion diffusivities in these materials.
- Use of the Nernst-Einstein equation to estimate ionic mobilities from the measured diffusion data.

Accomplishments

- Successfully developed a novel method of preparing lanthanide carbides by sintering lanthanum oxide/carbon admixtures heated to very high (>2500°C) temperatures using electron beam heating.
- Successfully stabilized La-Er carbide, La-Ce carbide and La-Y carbide produced with carbon-13 so that these compounds retain the cubic fluorite structure in the temperature range from 300 K - 2800 K.

Future Directions

- Complete the carbon-12 in-diffusion heat treatments.
- Determine the in-diffused carbon-12 depth profile using secondary ion mass spectrometry.
- Calculate the carbon ion mobility using the Nernst-Einstein equation.

Introduction

Carbon-consuming fuel cells have many potential advantages, including increased efficiency and reduced pollution. A large amount of work has already been done on coal fuel cells which utilize yttria-stabilized zirconium carbide as an oxygen-ion superionic membrane material. However, no superionic membrane material for carbon ions is yet known. Such a solid-state superionic membrane material would enable an entirely new class of carbon fuel cell to be developed that would use coal directly as the fuel source, without any intervening combustion process. A carbon-ion superionic conductor would be an enormous step forward because it would allow the direct conversion of coal to electricity without the formation of any of the pollutants (SO_2, etc) other than CO_2 that can accompany coal combustion. Fuel cells utilizing yttria-stabilized zirconium may require combustion of coal to carbon monoxide prior to final oxidation to carbon dioxide with the oxygen-ion membrane. The objective of this research is to investigate specific ionic lanthanide carbide and ionic lanthanide carbide pseudo-binary solid solutions as possible superionic carbide-ion conductors. The discovery of such a material would have the potential of ushering in a truly revolutionary new coal technology.

Rare earth carbides have the fluorite structure when they are above their transition temperatures, which vary from 350°C (EuC_2) to 1450°C (LuC_2). This structure is perhaps the crystal structure most widely found in superionic materials. These cubic lanthanide carbide compounds could potentially be good ionic conductors for carbon.

Approach

Rare earth carbides of the form LnC_2 (where Ln refers to any element of the lanthanide series) are being investigated as potential superionic membrane materials. These compounds have the fluorite structure when they are above their transition temperatures. The carbon atoms in these compounds reside as anions in tetragonal positions equivalent to the positions of the mobile ions F- and O_{2-} in the known superionic conductors CaF_2 and $Zr_{0.8}Y_{0.2}O_2$. Rare earth carbides represent perhaps the most favorable class of superionic carbon membrane materials. However, it is necessary to stabilize the cubic fluorite structure which these compounds exhibit at elevated temperature so that this structure is stable down to room temperature. Such stabilization is being sought by alloying rare earth carbides with substantially different lattice parameters. Measurement of carbon ion diffusivity will be measured via the in-diffusion of carbon-12 into the base carbide compound produced with carbon-13.

Results

The lanthanide dicarbides have been synthesized by reacting mixtures of Ln_2O_3 and amorphous ^{13}C under vacuum at high temperatures (>1600°C), using a newly developed synthesis technique which we have termed the reactive oxide electron beam (REOB) synthesis technique. These dicarbides were subsequently densified at high temperatures (<2500°C) using electron beam heating. Direct production of these materials by means of direct melting of lanthanide-series metals and carbon using water-cooled copper hearth arc-melting was found to be ineffective due to the uncontrollable dispersion of the carbon as a result of the arc blow generated by the high arc current.

La-Er carbide, La-Ce carbide and La-Y carbide have been successfully produced using the REOB procedure. Powder x-ray diffraction was used to confirm that their crystal structures remained stable in the fluorite structure in the temperature range of 300-2800 K. These compounds have been produced with carbon-13 in order that vapor-deposited carbon-12 coatings could be used in the diffusion measurements, since carbon-13 arcing electrodes or sputtering targets do not appear to be available from any source world-wide. Either arc evaporation or sputtering is needed to produce an adherent film for the high-temperature in-diffusion treatment.

Semi-thick coatings (>10 m) of ^{12}C were deposited on these samples using the arc-evaporation of high-purity, commercially available graphite electrodes. Natural graphite contains ~1.11% carbon-13 and 99% carbon-12. The small (1%) amount of carbon-13 contained in the graphite can be readily accounted for mathematically in the deconvolution of the measured carbon-12 in-diffusion profile. To produce these samples, coated samples are heated at 850°C, 950°C, and 1150°C in a custom-built high-vacuum furnace. Prolonged SIMS sputtering will be used to determine the complete carbon-12 diffusion profile from surface to baseline. From these measurements, together with semi-infinite diffusion equations, the carbon-12 diffusion constant can be determined, which can then be used in the Nernst-Einstein equation to calculate carbon ion mobilities.

Conclusions

- A novel method for preparing lanthanide carbides by sintering lanthanum oxide/carbon admixtures heated to very high (>2500°C) temperatures using electron beam heating has been developed.

- Stabilized La-Er carbide, La-Ce carbide and La-Y carbide have been produced with carbon-13 so that these compounds retain the cubic fluorite structure in the temperature range from 300 – 2800 K.
- Diffusion measurements together with the Nernst-Einstein equation will be used to determine the carbon-ion mobility in these fluorite structure stabilized lanthanide carbides.

FY 2004 Publications/Presentations

1. *Carbon Ionic Conductors for Use in Novel Carbon-Ion Fuel Cells*, Presented at the University Coal Research Contractors Review Conference, June 9-10, 2004, Pittsburgh, PA